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Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants

THIS ISSUE

The Electron Microscope in the Petroleum Industry

PUBLISHED BY
THE TEXAS COMPANY
TEXACO PETROLEUM PRODUCTS

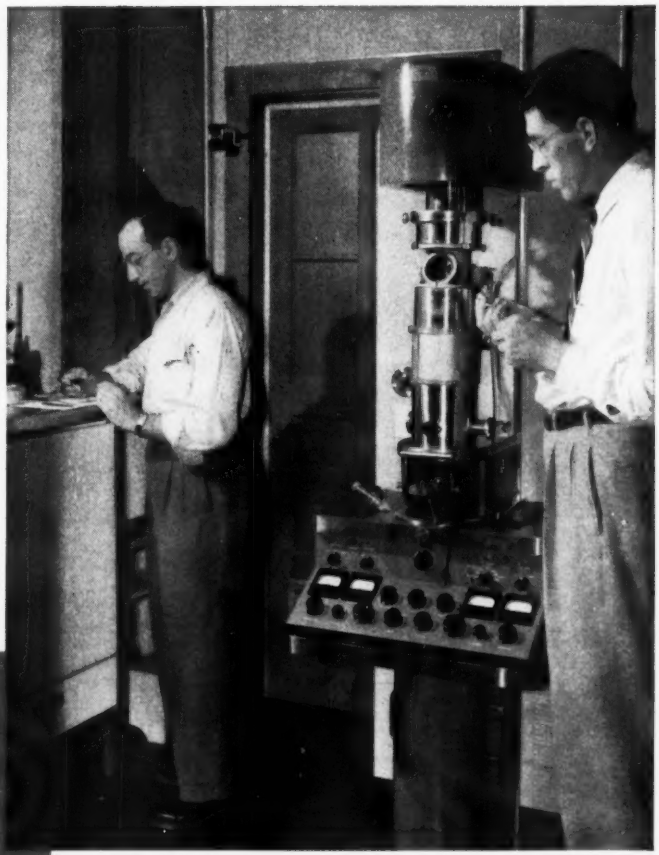
I dipt into the future

far as human eye could see,

Saw the vision of the world

and the wonder that would be.

TENNYSON: LOCKSLEY HALL



EYE TO THE FUTURE

Electron Microscope in the Beacon Laboratories of The Texas Company, Beacon, N. Y. A specimen for study is being prepared by man at left. His fellow worker is about to put a specimen into the microscope.

It is written large in The Texas Company's credo that today's best product must be merely a stepping stone to tomorrow's better one. Texaco scientists are always looking ahead.

One important eye to the future is the electron microscope—whose superhuman ability to peer into the basic structure of petroleum products is outlined on the following pages. Used in conjunction with chemical analyses, X-rays, light diffraction and other "eyes", the electron microscope "sees" essential things hidden from unaided human sight . . . enables Texaco scientists to see how better oils and greases can be developed.

So Texaco is always ready when new needs for lubricants arise. Tomorrow, as today, industry will benefit by the outstanding ability of Texaco Industrial Lubricants and Lubrication Engineering Service to maintain the efficiency of machines and equipment and to bring down the unit cost of production.

TEXACO REG. T. M.

THE TEXAS COMPANY

LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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The Electron Microscope in the Petroleum Industry

OF THE many and varied developments in electronic instruments during the past two decades, probably no instrument has caused more widespread interest and awe than the electron microscope. Other instruments generally provide data which cannot be appreciated until the records have been analyzed and interpreted by experts. Often the theories involved are quite complicated. In contrast, electron micrographs are often full of meaning even to the inexperienced observer.

Through pictorial representation, the electron microscope has extended the powers of direct visual observation and made it possible to almost completely fill the gap between those objects that are seen by the light microscope and the larger molecules. It is one of the most important new tools of research because, in a most extraordinary way, it has increased our ability to see directly into the fine structure of matter.

The electron microscope is a tool that can be applied to any field of scientific investigation where the physical properties of size, shape, and structure of single particles and the state of aggregation of particles in the colloidal range, 0.5μ to 0.001μ (1 micron, μ, is $\frac{1}{10{,}000}$ cm or $\frac{1}{25{,}000}$ inch), are important.

LIMITATIONS OF THE LIGHT MICROSCOPE

Theory and experiment have shown that there is an absolute and unalterable limit, set by the wavelength of light on the size of what can be seen. By the use of visible light, which has a wavelength of about 0.5μ, we could never hope to see* anything smaller than about 0.2μ. If we use invisible ultraviolet light and record the image on a photographic plate, we can portray objects about half this size.

To see things smaller than the limit set by visible or ultraviolet light requires then that we find another kind of illumination, a radiation of shorter wavelength. We have known about the short wavelength of x-rays since early in the century, but no one has yet found a completely satisfactory way to focus x-rays to form an image in the manner that glass lenses focus light.

DISCOVERY OF THE PRINCIPLES OF THE ELECTRON MICROSCOPE

It was fortuitous, then, that two important developments of the 1920's came to our rescue. A French scientist named de Broglie developed a theory (1924) that every moving body has a wave character associated with it, and the faster the body moves the shorter the associated wavelength. We knew at this time how to make electrons move at high speeds, and it was only a short while until Davisson and Germer performed an experiment showing that

* Light scattered from particles as small as 0.001μ can be seen in the ultra-microscope or the dark field microscope, but the particles themselves are not seen.

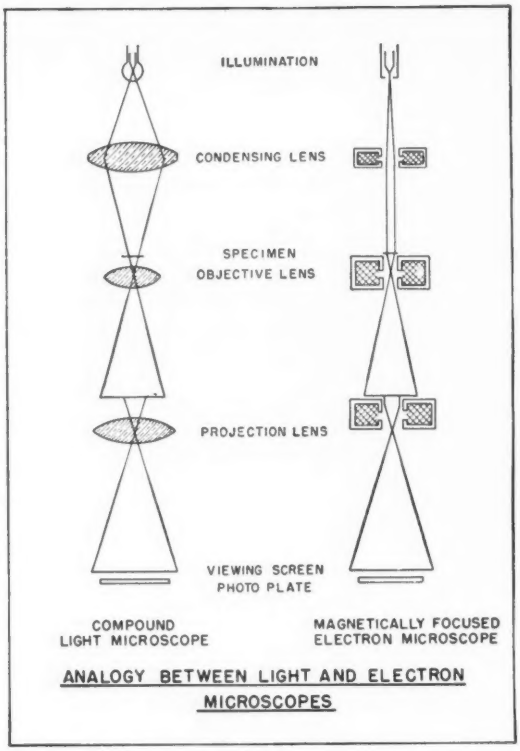


Figure 1

under certain circumstances high velocity electrons behave like light waves.

The extension in vision that becomes theoretically possible by illuminating with an electron beam is very great. Electrons moving with velocities corresponding to a few tens of thousands of volts have wavelengths nearly a hundred thousand times smaller than the wavelength of visible light. In fact, the wavelength of the radiation used in present day electron microscopes is less than 0.05A (1 angstrom, A, is equal to $\frac{1}{10{,}000}$ micron, μ). An electron microscope that could use to full advantage these extremely short wavelengths could penetrate deeply into the structure of individual atoms. It is not now possible, however, to take full advantage of such short wavelengths and we do not yet see how it can be achieved.

Anyway, electron microscopes and specimen preparation techniques have been developed to the point that particles less than 10A across can be portrayed. This two hundred-fold extension of vision opens an important new world of objects to direct observation and study.

The second important discovery of the 1920's that made possible the practical use of electrons for illuminating objects was that of H. Busch in Germany in 1926. He showed that a properly shaped magnetic field could be used as a lens to focus a beam of electrons in much the same way that a properly shaped piece of glass focuses a beam of light. The magnetic field bends the path of an electron beam as a glass lens bends the path of a light beam.

Several years passed, however, before the first crude electron microscope utilizing these principles was built. But by 1939 the development had reached a stage where a model bearing all of the essential elements of the most modern electron microscope was being manufactured in Germany. While improvements have been made on the microscope since 1939, more effort has gone into developing the techniques of using this new and valuable instrument.

In order to understand what an electron microscope can do, it is necessary to know how the microscope is built and how it works. The possible applications of the electron microscope are so numerous and so unpredictable that even at this time little can be said besides pointing out the kinds of objects that can be examined and how the object or specimen is prepared for examination.

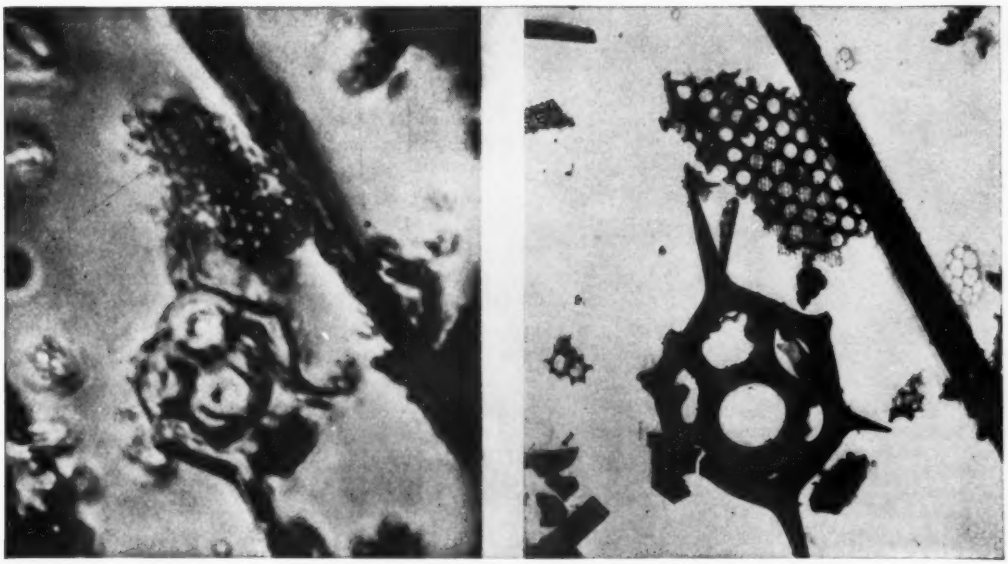
DESCRIPTION OF THE ELECTRON MICROSCOPE

Like the light microscope, the electron microscope consists of an illuminating system, a specimen stage, an imaging system and a camera. Yet, in its physical structure it is anything but similar to the light microscope. The reasons are simply manifestations of the fundamental differences between electrons and light.

Electrons are readily stopped or scattered by all forms of matter, including air. It is therefore necessary that the entire electron beam be kept in a vacuum chamber. For producing and maintaining the necessary high vacuum, adequate pumping facilities must be provided.

The electron microscope must also include a number of highly regulated electrical power supplies for the production and control of the electron beam that illuminates the specimen and forms the image in the camera.

In a typical electron microscope, the electrons emitted by a hot tungsten filament are accelerated as a beam to a high velocity. This high velocity electron beam passes into the optical system of the microscope where it is first focused upon a suitably prepared specimen by the condensing lens. Some of the electrons in the beam are absorbed by the specimen. Others are scattered out of the beam and also lost. The number of electrons being absorbed or scattered depends upon the density or thickness of the specimen at each point. One can see, then, that the manner in which the remaining electrons are



Light Micrograph *Courtesy of Radio Corporation of America* Electron Micrograph

Figure 2 — DIATOM FRAGMENTS X 3000. Micrographs showing image defects when the limit of resolution of the optical system is approached.

distributed in the beam is determined by the details in the specimen.

As the electron beam passes through the magnetic field of the objective lens it is brought to focus as an enlarged primary image. A portion of the electrons in this image are brought to a second focus by another lens, the projection lens, on a fluorescent viewing screen or on a photographic plate where the electrons interact with the photographic emulsion to produce a permanent record of what was seen on the fluorescent screen.

The electron lenses—the condenser, the objective and the projection lens—are the magnetic fields of three iron core coils. Unlike the optical microscope in which the strength of a lens is fixed and an image is brought into focus by changing the location of the specimen, the specimen location remains fixed in the electron microscope and the image is brought into focus by changing the strengths (focal lengths) of the lenses. This is accomplished by increasing or decreasing the electric currents in the coils thereby changing the strength of the magnetic fields of the electron lenses.

The specimen is supported on a thin plastic film stretched across a small disk of 200-mesh copper screen. (Figure 3). The plastic film is structureless and thin enough that it does not interfere appreciably with the passage of the electron beam. A suitable collodion film is about 100A thick. The prepared specimen on the specimen grid is supported in the electron beam on a movable stage, the location of which can be controlled by the operator. The focused image of a selected specimen area is photographically recorded on either a lantern slide or photographic film.

The foregoing briefly describes the electromagnetic type electron microscope. While microscopes have been built which utilize electrostatic fields to obtain image formation, these microscopes have not been as widely used as the electro-magnetic type. Typical of this latter group of instruments are the RCA Types EMU and EMT (United States), the Philips (Holland), the Metropolitan Vickers EM3 (England) and the Siemens UM100 (Germany) electron microscopes.

APPLICATION OF THE ELECTRON MICROSCOPE

The uses to which the electron microscope can be put and the problems it can best solve are in general of two different types. One group of prob-

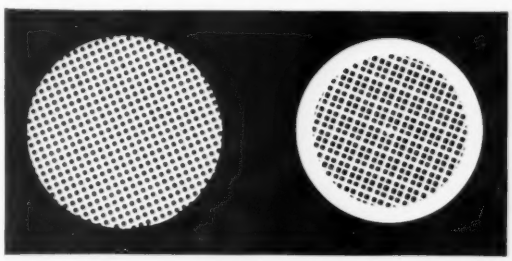


Figure 3 — The specimen is supported on a very thin (100A) plastic film stretched across ⅛″ disks of 200-mesh screens. At the right is a special screen of English make that has a center mark to help the microscopist locate specific areas on the specimen.

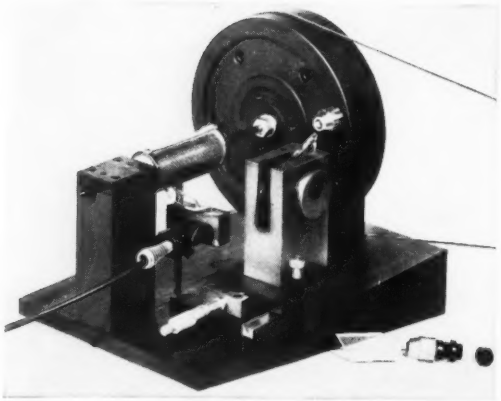


Figure 4 — The ultramicrotome, a specialized form of slicing machine, is used in preparing thin sections of soaps and the softer solids for examination in the electron microscope. The ultramicrotome shown here was designed and built at the Beacon Laboratories of The Texas Company and follows a design suggested by Dr. James Hillier of the Radio Corporation of America.

lems includes those that have already been investigated by optical microscopy but for which the higher magnification of the electron microscope can reveal additional information about fine structure. Constituting the major field of application of the electron microscope, this category includes such problems as particle size determination for dusts, smokes, pigments and colloidal suspensions, the examination of metallographic specimens and the study of the surface structure of all kinds of solids. The value of the new information that has been turned up in these investigations cannot be underestimated. In some instances the information has been of immediate economic value. In others it has contributed significantly to long range research programs that are already paying off. One such type of program is lubricating grease research. The other set of problems are concerned with the molecular components of matter and are of considerable fundamental importance. They are interesting and intriguing because, for the first time, we are able to measure and to see some of those components of matter previously known only indirectly. All of the bigger molecules that are now visible for study are of organic origin or composition. The ability to see separate molecules may, in time, lead to the development of a visual chemistry wherein the effects of the interaction of molecules in the physical as well as the chemical sense can be observed on a molecular scale.

The application of the electron microscope to solving some of these problems predicates (1) suitable preparation of the specimen for examination, (2) examination of the image of the specimen on the fluorescent screen and (3) preparation of the electron micrograph, a record of what was seen.

Specimens of Materials Must be Especially Prepared for The Electron Microscope

A disagreeable characteristic of electrons when used to illuminate a specimen is their extreme readiness to be stopped by all forms of matter. This imposes two limitations. In electron microscopy there is the requirement that every examination be carried out in a vacuum. This means that every specimen must be completely dessicated. Then, due to the opacity of matter for electrons, every specimen must be prepared so that not all of the electrons in the beam are absorbed by the specimen. If the specimen consists of dust particles, the individual particles must be separated and in a layer no more than one particle thick. If the specimen is continuous as a film or section it must be no thicker than a few tenths of a micron.

Whatever is done to prepare a specimen for electron microscope examination, however, must not so alter it that the desired information is lost or masked by details that are not inherent in the sample from which the specimen was taken. Experience has shown that specimen preparation is the most important aspect of electron microscopy and often taxes the imagination and ingenuity of the microscopist.

Most Specimens are Solids

The vast majority of specimens are solids in some form. They may be compact, particulate or in colloidal suspension. The surface of metallographic sections, of crystals, of bearings or other wear surfaces are examples of compact solids. Dusts, smokes,

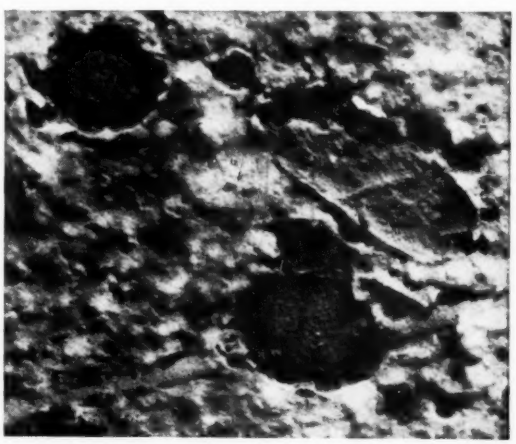


Figure 5 — Formvar negative replica of the polished and etched surface of an aluminum alloy piston. The areas of the metal surface that are resistant to etching appear as depressions or craters in the electron micrograph of a negative replica. Such areas are metal alloy inclusions and the boundaries between metal grains. Here are seen the nearly circular areas that represent $AlMn_3$ inclusions.

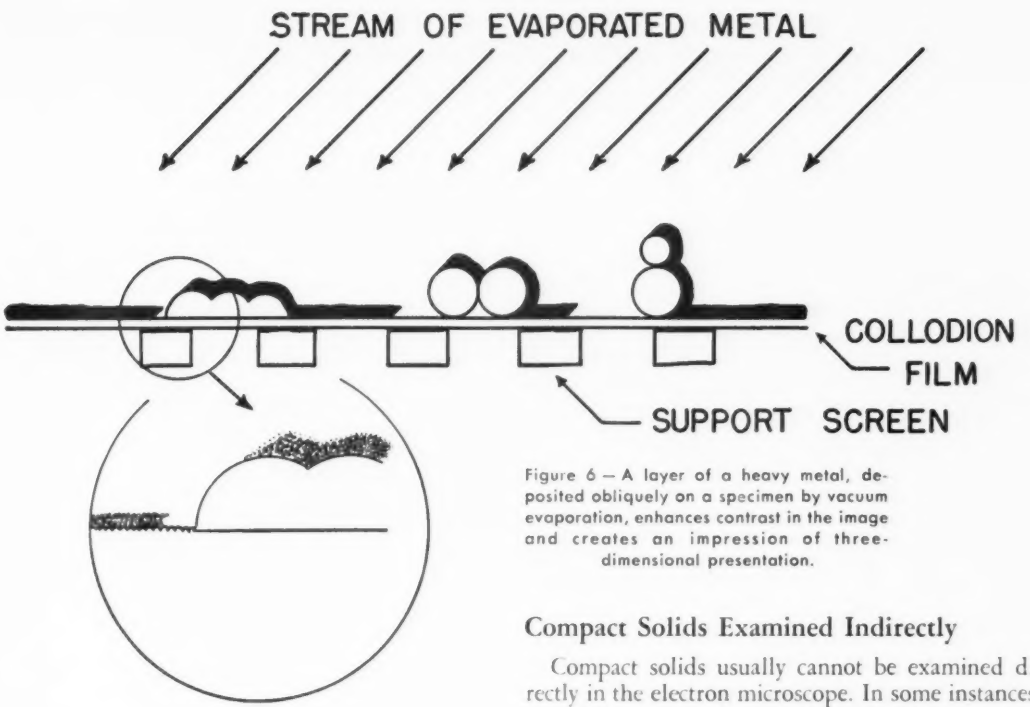


Figure 6 — A layer of a heavy metal, deposited obliquely on a specimen by vacuum evaporation, enhances contrast in the image and creates an impression of three-dimensional presentation.

pigments, catalysts and clays generally are found as particles or groups of particles. Soap fibers and certain additives in oils represent solids in colloidal suspension.

Finely divided solids or particles in suspension are generally the easiest specimens to prepare for examination. If they are dry and do not stick together they are merely dusted onto an extremely thin plastic film which is stretched over a 1/8 inch disk of 200-mesh screen. The screen, which is the specimen support, is then ready for positioning in the electron beam and for examination.

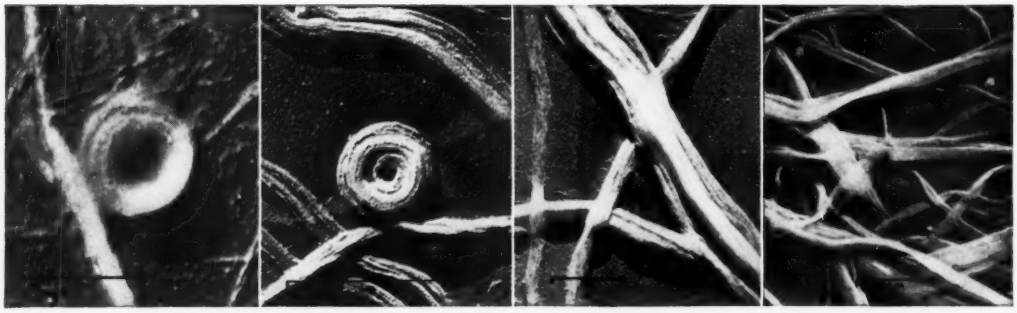
When the particles are suspended in oil or water, these liquids must be removed before the specimen is examined. The water readily evaporates when the electron microscope is evacuated, but, because of their low vapor pressures, oils may evaporate only very slowly if at all. When the oil is not removed from the specimen, it must be present only as an extremely thin film, so thin that the electron beam can pass through it with no noticeable scattering. Even then, miniscuses of oil form around the edges of otherwise sharply defined particles giving them a fuzzy appearance. It is sometimes possible to remove the oil from a specimen before it is put into the microscope. The most simple method is that of carefully washing or leaching the sample with a suitable light solvent. However, considerable care is taken to avoid changing the state of aggregation or other physical properties of the particles when the oil is removed.

Compact Solids Examined Indirectly

Compact solids usually cannot be examined directly in the electron microscope. In some instances, especially with soft materials, ultrathin slices of the solid are cut with a slicing device called a microtome. (Figure 4). The slices, or thin sections, however, must not be more than about 0.1 micron thick.

Generally only the specially prepared surfaces of compact solids are studied by electron microscopy. No really satisfactory method of directly examining these surfaces by electron microscopy has been developed, however, and only indirect methods of examination are used. These indirect methods include all of the various replica techniques. In its simplest form the replica technique consists of pouring a dilute solution of a plastic material like collodion onto the solid surface. When the solvents have evaporated there remains on the solid surface a very thin plastic film. When the film is peeled from the surface there will be on one side a roughness that will be a faithful replica of that surface. The other side of the film will be relatively smooth. The variation in thickness of the replica, because of the roughness on one side, results in variations in opacity to the electron beam when the replica is examined in the miscroscope. The image of the replica will then be a topographic map of the solid surface and, if it has been shadowed, every hill and valley stands out with remarkable clarity.

Electron microscopy of metal surfaces through the use of the replica technique has provided much fundamental knowledge about crystallization, grain growth, alloy formation and structure (Figure 5). In some laboratories these techniques are being



A B C D

Figure 7 — Electron micrographs of four sodium soap greases showing some of the relations between soap composition, oil viscosity and oil quality. a) Sodium tallowate in high concentration, crystallized in a waxy residual oil, is composed of particles and poorly formed fibers. b) When the grease from which the fibers shown in (a) were taken is diluted with a better grade of oil and recrystallized, long hank-of-hair type fibers are formed. c) Sodium tallowate crystallized in highly refined oil is composed of more uniform fibers. d) The widths of sodium myristate fibers, composed of hair-like fibrils, fall within narrow limits. Closed loops and "doughnuts" seem to be characteristic of the sodium soap fibers.

applied to the study of friction and lubrication.

The techniques just described are also being applied with some success to the field known as chemical microscopy*. The formation of precipitates, the effects of acidity upon crystal growth and similar problems have been investigated. It is not yet known, however, how widely this type of chemical microscopy can be used.

Shadowing Improves Contrast

Often particles are difficult to discern because they do not scatter many more electrons than the plastic film on which they are supported. Aside from reducing the thickness of the supporting film, scattering from particles can be increased by covering them preferentially with heavy metal atoms.

* R. B. Fisher, Trans. Ill. State Acad. Sci. 38, 74 (1945).

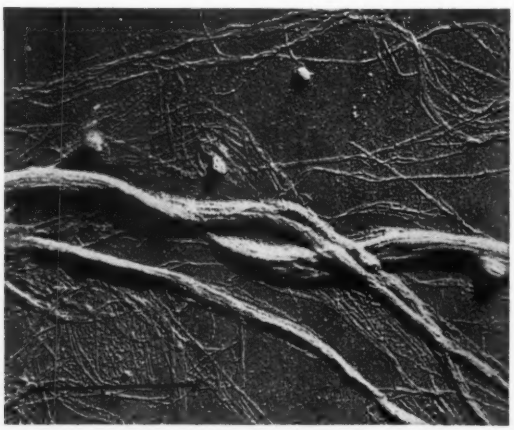


Figure 8 — The fibers of a shear-stable sodium soap grease are split upon working into finer fibrils. These fibers originally looked like those shown in Figure 7 (b).

If the metal deposit is made obliquely a metal film will result which varies in thickness according to the extent the specimen projects above the surface of the supporting screen. To the illuminating electron beam, then, the specimen will vary in opacity according to the thickness of the deposited film.

This technique, called shadowing or shadow casting, requires the high vacuum evaporation of an extremely small amount of metal. The metal atoms travel in straight lines in all directions from their source and condense upon whatever they strike. The thickness of the metal film so produced will be greatest on those surfaces facing the oncoming atoms, and those regions of the supporting film lying behind high detail will be shielded and receive no metal (Figure 6). These clear regions appear to be shadows when the specimen is viewed in the microscope. The variations in opacity that result from variations in the thickness of the metal film create an impression that one is seeing the specimen in three dimensions illuminated by light coming from the same direction as the shadowing atoms.

Shadowing was originally devised as a means of determining the heights of electron microscope objects through measurements of the lengths of the shadows they cast, but the increased contrast and three-dimensional presentation have out-weighed the original purpose of this technique. Unfortunately, however, shadowing masks the internal details of semitransparent objects.

Although many problems of technique remain in electron microscopy, the existing methods now permit reliable and convenient observation of most materials and furnish the investigator with a base from which he can, with a little ingenuity, proceed to develop new preparative methods suited to specific specimens and problems.

LUBRICATING GREASES CONTAIN FIBROUS SOAPS

A conventional lubricating grease is a suspension of the fibers of a metal soap in a lubricating oil. The soap fibers uniformly distributed throughout the oil, act like a felt pad holding the oil principally by capillary attraction between the soap fibers. The metal soaps most commonly used in grease making are those of sodium, calcium and lithium. These soaps crystallize in long, thin fibers having a shape characteristic of the metal atom and a size determined by the fatty acid comprising the soap (Figure 7). In a few instances greases contain metal soaps, such as aluminum stearate, which crystallize only as extremely fine particles.

It was known in the late 1930's, through the use of the optical microscope, that many grease soaps were fibrous. Rough estimates had been made of the lengths of some of these fibers and correlations were drawn between the estimated fiber lengths and the consistency of the parent grease. In these studies, however, nothing was learned of the width, thickness or surface structure of the fibers.

During the last decade tremendous progress has been made, through the use of the electron microscope, in the characterization of soap structures and in the correlation of these structures to the physical properties and behavior of the greases. Early estimates of length were confirmed. Widths and thickness have been accurately measured. Differences in surface textures have been discovered.

We now use such terms as hank-of-hair, two-strand rope, and twisted ribbon to describe the various ways in which the soap micelles or fibrils get together to make the familiar soap fibers.

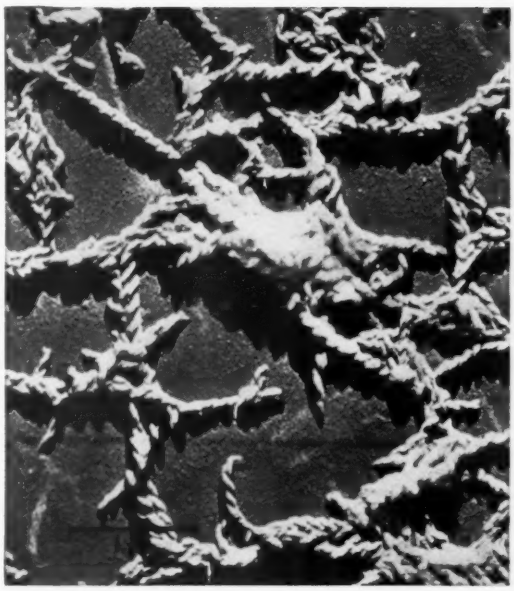


Figure 10 — The two-strand rope-like fibers of calcium tallowate are characteristic of cup greases.

It appears that in nearly every instance the fibers of the sodium soaps of fatty acids are composed of hair-like fibrils assembled into parallel aggregates resembling hanks-of-hair. When a grease containing these hank-of-hair fibers is subjected to shearing action as in a roller bearing, the fibers are split into their constituent fibrils (Figure 8). Although the fibrils may also be broken into shorter pieces, the grease retains its physical properties because a high length-to-width ratio in the soap

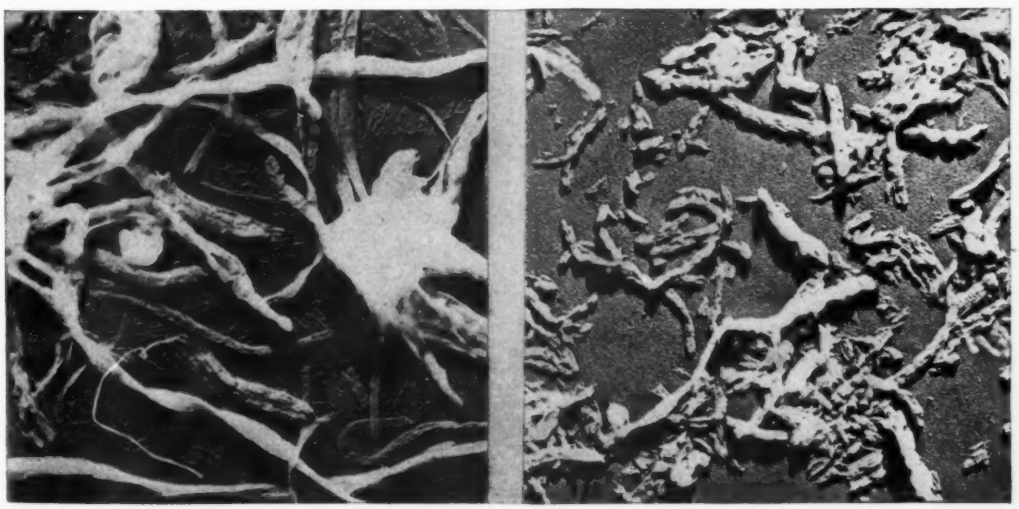


Figure 9 — The fibers in a sodium soap grease that is not shear-stable will have many transverse fissures in them. When subjected to shearing action, the fibers are broken along the fissures.

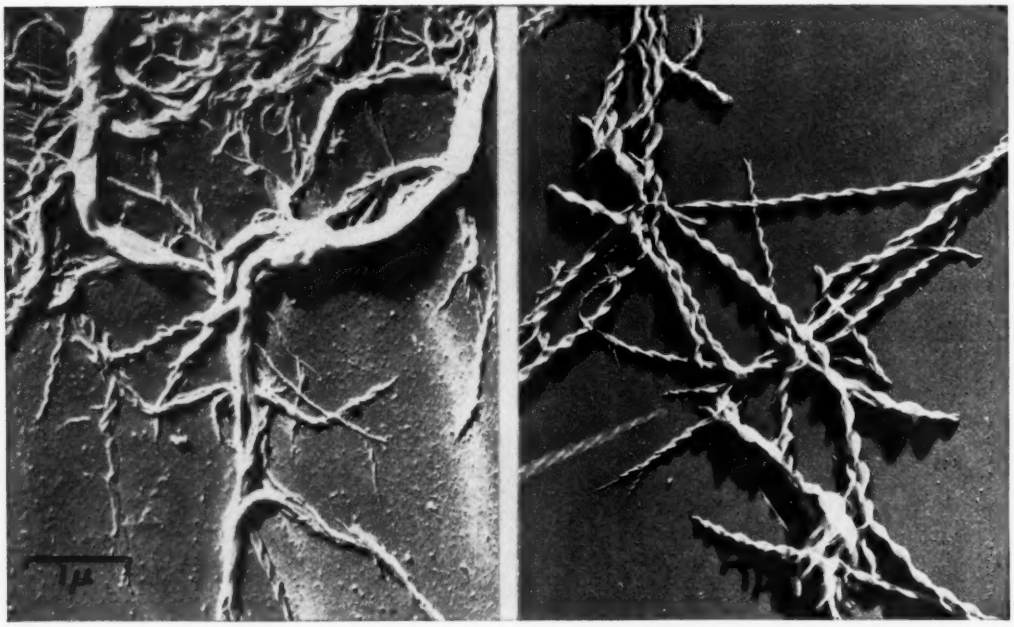


Figure 11 — The quality and uniformity of the soap fiber depends on the purity of the fatty acid used in its manufacture. Prepared from hydrogenated castor oil, the soap fibers at the left are composed of lithium 12-hydroxystearate (85%) and lithium stearate (12%) and may contain glycerine. Those at the right were prepared from the methyl ester of 12-hydroxystearic acid and are nearly pure lithium 12-hydroxystearate.

fibers is retained.

It is possible to prepare a sodium soap that does not have hank-of-hair fibers. The fibers will appear more ribbon-like but will have many transverse fissures in them. When greases containing such fibers are subjected to shearing action the fibers are broken along the fissures (Figure 9). Because the resultant soap particles do not retain a high length-to-width ratio the consistency and other properties of the grease are radically changed.

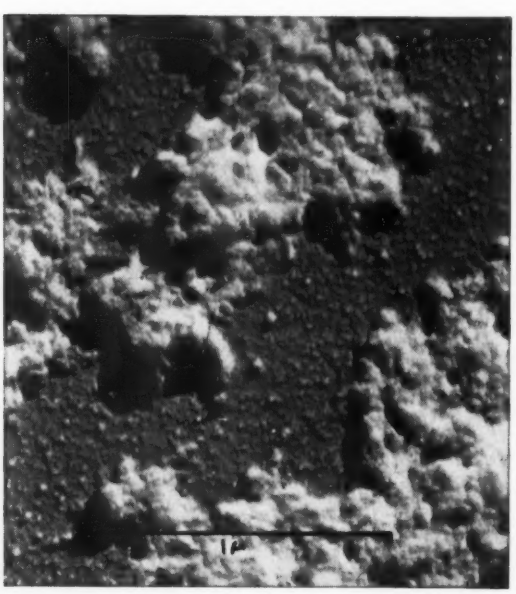


Figure 12 — Aluminum stearate greases contain only very small spheroidal particles.

Calcium soaps, under certain conditions, crystallize in fibers that have the appearance of two-strand ropes. In cup greases the calcium tallowate fibers are found to have a highly uniform width and constant rate-of-twist, or pitch (Figure 10). The twist of these fibers may be either left or right-handed and the lengths fall within rather narrow limits. When prepared from 12-hydroxystearic acid, calcium soaps have a right-hand twist, only. While the length-to-width ratio of these soap fibers is about the same as those of calcium tallowate soaps, they are generally much smaller.

Lithium soaps appear as twisted ribbons in many greases. These fibers are a few times wider than thick and may be many times longer than wide. In general the twist has a constant pitch, but not every fiber in a batch will be twisted either completely or regularly.

In many instances the quality and uniformity of a soap fiber depends on the purity of the fatty acid from which the soap is prepared (Figure 11). The fibers of lithium soap prepared from high purity 12-hydroxystearic acid are highly uniform in width and have a regularly twisted structure. Those prepared from hydrogenated castor oil are

irregular in width, twist and surface smoothness.

It has been shown that in some instances a satisfactory grease is not formed unless the soap and oil are combined above a certain temperature. The electron microscopic examination of these soaps reveals that the high temperature product is composed of fibers while the low temperature product is composed of irregular particles having the widths about equal to the lengths. Satisfactory greases can be made, however, which contain the soap in a particulate form. In a calcium resinate grease, axle grease, and in the aluminum stearate greases the soap particles are fine spheroidal particles (Figure 12). They are so fine that it is difficult to determine their dimensions, even under the electron microscope.

Just as it is possible to make greases containing the soap in the form of fine particles, it is also possible to make greases containing other kinds of fine particles (Figure 13). The electron microscopic examination of a number of greases containing finely divided solids such as clays, silica, and certain pigments has shown that when the average particle size of these powders remains below a certain value, gelling action will take place and a stable grease will be formed. If these dimensions are exceeded the particles settle out of the oil and no grease is formed (Figure 14).

In spite of the remarkable contribution electron microscopy has made to the science of grease making, innumerable problems still remain upon which these techniques of investigation can be brought to bear. A full understanding of many problems, such as the mechanics of fiber formation, will not be gained by electron microscopy alone, however. To the information obtained through the use of the electron microscope must be added the information from all of the other applicable tools of research which yield structure data.

Figure 13 — Attapulgite, a clay mineral from Attapulgus, Georgia, which when treated with a wetting agent is used in making non-soap greases.

PARTICLES IN FUELS AND LUBRICATING OILS

A field of investigation in which there is growing interest is the examination of crude petroleum and

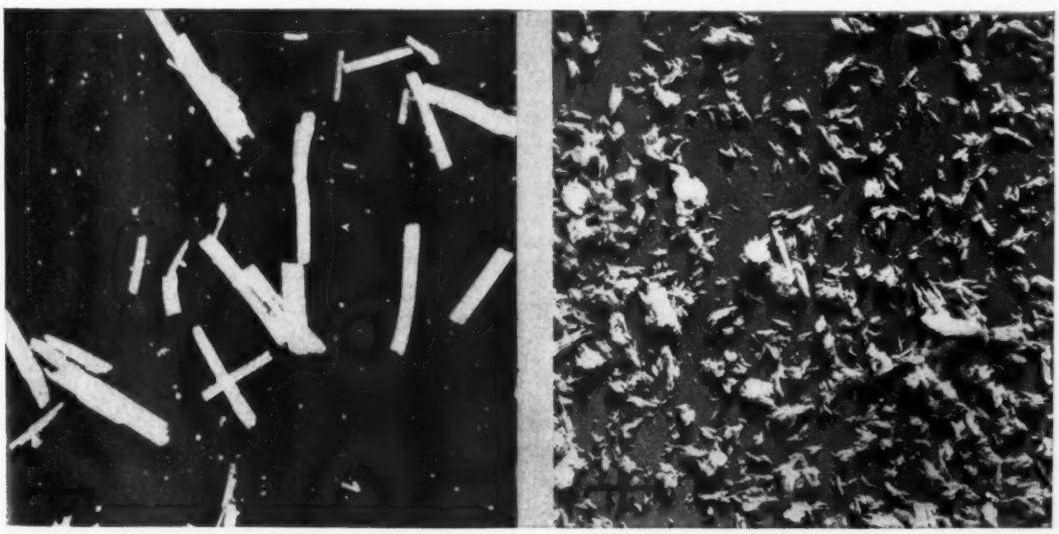


Figure 14 — Organic pigments used in making special purpose greases. When solid particles are too large, as in the Figure at the left, they settle out of the oil and no grease is formed.

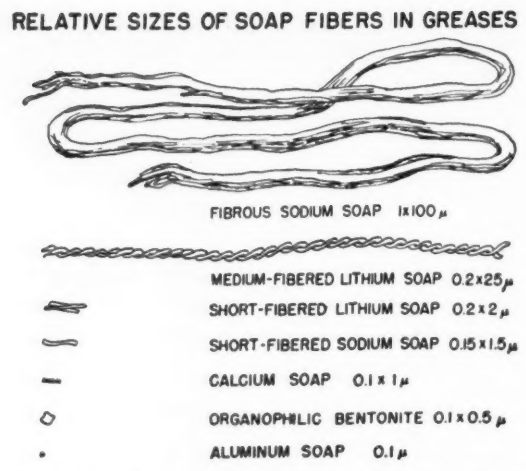

RELATIVE SIZES OF SOAP FIBERS IN GREASES
FIBROUS SODIUM SOAP 1x100 μ
MEDIUM-FIBERED LITHIUM SOAP 0.2x25 μ
SHORT-FIBERED LITHIUM SOAP 0.2x2 μ
SHORT-FIBERED SODIUM SOAP 0.15x1.5 μ
CALCIUM SOAP 0.1 x 1 μ
ORGANOPHILIC BENTONITE 0.1x0.5 μ
ALUMINUM SOAP 0.1 μ

Figure 15 — Redrawn from a chart by B. B. Farrington, Ann. New York Acad. Sci., 53, 979 (1951).

petroleum products for particles in suspension. As might be expected, however, the nature of the particles that may be seen depends to a large extent upon the composition and history of the specimen.

Crude oils are thought to be composed of asphaltic or bituminous micelles or particles, asphaltic resins and oil. The bitumen micelle may contain soot or graphitic carbon. Thin films of crude oil, however, show few if any particles when examined by electron microscopy. A specimen of crude oil diluted in a light solvent, on the other hand, shows[a] the presence of many globular, amorphous particles. These particles are apparently aggregations of the much smaller micelles, and the aggregation may have been caused by "breaking" the crude oil suspension by the solvent.

In the study of coal tar asphalts it was found[b] that when the surface tension of the solvent used in specimen preparation fell below a critical value coagulation of asphalt particles always occurred. By the use of a suitable solvent, however, specimens in which micelle aggregation did not take place were prepared and valuable data relating coal tar micellar size with binding power in briquettes and paving compounds were obtained. Studies of this type have not yet been made of asphalts derived from crude oil.

Finished petroleum products such as lubricating oils may be expected to contain in suspension many kinds of particles such as clay from various processing steps, organic crystals such as soaps and waxes, oxidation products that might contribute to varnish, lacquer or gum formation, additives in colloidal dispersion or "dirt" with absorbed additives. Used lubricating oils may also contain finely divided combustion and wear products such as carbon and iron or other metal particles. The possibility of seeing these particles and of correlating the particle dispersion pattern with the physical properties and behavior of the oil has lead to intensive research programs in many laboratories.

A few simple calculations involving the density of typical additives and the contrast limits in the electron microscope image indicate that additive particles as small as 200Å diameter may be seen in a suitably prepared film of oil. Already reports[c] have been made of the existence of "spherical" and rod-like micelles of detergent type additives in oils. These micellar particles are stated to have dimensions falling below 100A, confirming the simple calculations.

It has been suggested by some investigators that the efficiency of lubricating oil additives is reflected in the degree of particle dispersion maintained in the used oil. They contend that an effective detergent keeps small wear particles and combustion products from coagulating and settling out in the oil lines and elsewhere. Samples of highly detergent used oils taken from an engine at intervals over a period of several hundred hours show no pronounced differences in particle size or particle size distribution. (Figures 16, 17). From this it can be concluded that the additives in such oils are doing their duty. Techniques have not yet been worked out for counting the number of particles in a given

[a] G. W. Preckshot, N. G. De Lisle, C. E. Cottrell and D. L. Katz, Trans. AIME, Tech. Publ. 1514 (1942).

[b] A. K. Sarkar, Kolloid Zeits, *130*, 116 (1953).

[c] B. Peri, 124th National Meeting, American Chemical Society, Chicago, Ill., September 6-11, 1953.

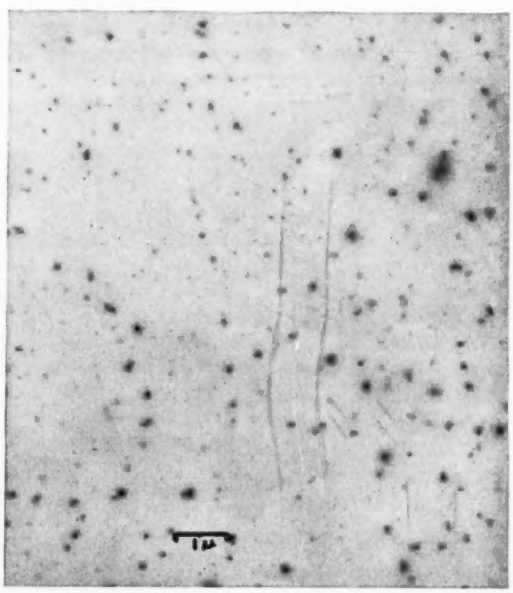


Figure 16 — Dispersion of particles seen in a thin film of lubricating oil after 300 hours use in an internal combustion engine.

volume of used oil. From such counts, however, it may be possible to learn something of the behavior of an internal combustion engine as, for example, the amount of carbon, formed in the combustion chamber, getting into the lubricating oil.

The electron microscopic examination of gasoline and fuels has hardly begun. It has long been known that sunlight has an adverse effect upon lead-containing gasolines, causing the precipitation of lead compounds. The individual chains of particles of which the precipitates are composed can readily be seen in the electron microscope. Other "particles" seen in specimens of gasoline or fuel oil are not so easily identified. Analytical tests on gasolines, such as the ASTM copper dish test, show either the presence of a certain amount of gum-like material or the tendency of a fuel to form such materials. While no work has yet been done in this field, it may be possible to correlate the electron micrographs of the non-volatile components of fuels with research data like that just mentioned. As can be seen, many problems in fuels research remain to be solved.

CATALYSTS PROVIDE MANY INTERESTING PROBLEMS

The effectiveness of a solid catalyst depends in a large measure upon the amount of surface per unit weight (or volume) the catalyst presents to the components of the chemical reaction. High surface area is obtained only in very porous or very finely divided solids. The particle size of catalyst preparations, therefore, generally falls into the range of the electron microscope. A study of the various solids that are useful as catalysts shows that many of them are amorphous. That is, they are composed of particles so finely divided that they appear no longer to be crystalline when examined by conventional methods of x-ray diffraction. Such materials include silica gel, activated alumina, cracking catalysts, colloidal platinum, platinum sponge, iron and nickel powders prepared from the corresponding oxides and from the carbonyls, vanadium pentoxide gel, asbestos, kaolin, and bentonite clay, activated charcoal, tungsten oxide and the catalyst supports like kieselguhr and infusorial earth. Some of these particles are spherical or irregular while others are plate-like and still others are definitely fibrous or thread-like.

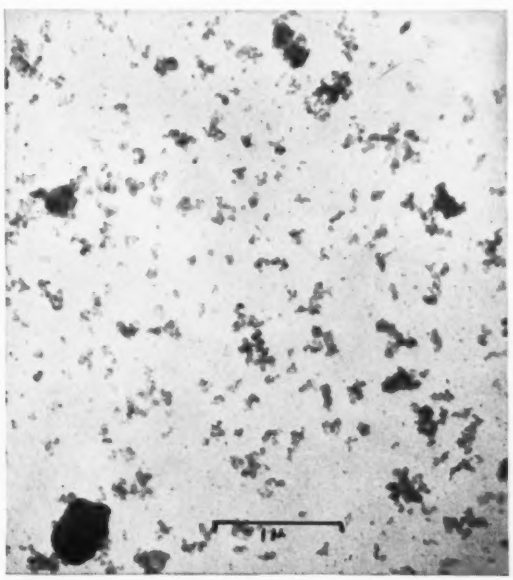


Figure 17 — On removing the oil from a thin film of used engine lubricant, the dispersion of particles is seen more clearly and found to resemble the carbon particles formed when hydrocarbons are incompletely burned.

The development of the electron microscope affords an opportunity to study the form and structure of these catalytic solids. Their particle sizes range from about one micron (10,000A) on the large side to near the limit of resolution of the electron microscope (15A) for the smallest particles. It has been reported that the particles in platinum sol are as small as 15 angstrom units in diameter while the particles in platinum sponge are between 50 and 100 angstrom units across.

Sols and suspensions of catalysts composed of one phase (e.g., a metal or metal oxide) are relatively easy to examine by electron microscopy. When the suspension is composed of two or more phases as in supported catalysts, however, it is often hard to differentiate one phase from another. Some supported catalysts are readily examined, though, because they are composed of an easily recognized dense particle on a less dense supporting particle or fiber. Platinum or palladium precipitated on asbestos fibres and platinum on charcoal are examples of these catalysts.

Other catalysts can be studied only with difficulty. The granular catalysts must be broken apart and separated into their ultimate particles or crystallites without too seriously altering the structure of the particles. With some amorphous materials with high surface area this cannot be done. Calculations of surface area from the particle size, then, do not agree with the surface area calculated from gas adsorption measurements. The difference is a measure of the internal surface of the catalyst.

Many catalysts are prepared by the reduction of metal oxides to the metal. Electron microscopic examination of the oxide particles and of the metal particles shows that the metal particles are much smaller than their parent oxide particles. This sintering effect is very much less when promoter substances like potassium carbonate are present while the reduction is taking place.

When one wants to understand what happens on the surface of a catalyst particle after it has taken

part in a chemical reaction, he must, somehow, see what has happened between the atoms involved in the reaction and the atoms of the catalyst particle. Electron microscopy cannot be used to watch the interaction while it is going on, but it is possible to examine a dispersion of particles in the before and after states by the simple expedient of supporting the catalyst particles on a film that will not be damaged during the reaction. Silica or alumina films may be used instead of collodion.

From such studies one can make deductions regarding the role of the catalyst in a chemical reaction. He can also learn something about the changes that take place on the catalyst surface that change its activity. Important results have been obtained by such methods on the formation of carbon on the surface of cracking catalysts and on other catalysts.

Another approach to understanding how a catalyst works is through the study of large single crystals of metals that have catalytic properties. It has been found that when single crystals of copper or nickle have been used as catalysts, pronounced changes take place on some parts of the crystals while other parts are hardly affected. The electron microscopic examination of the crystal surfaces by replica techniques may soon reveal the differences that make some surfaces more active than others. Such investigations are still in their infancy.

OTHER USES OF THE ELECTRON MICROSCOPE

Electron Diffraction

Many electron microscopes are so constructed that they can be easily converted for the production of electron diffraction patterns. The analysis of crystalline substances by electron diffraction (as with x-ray diffraction) is a large subject in itself and cannot be considered a part of electron microscopy. There are many instances, however, where correlation of diffraction data with the electron micrograph has been of great value.

In general, electron diffraction patterns are made from extended areas of a compact solid or from a thin layer of a powder. More recent developments in electron microscopes have provided a means of isolating the diffracted radiation from individual particles in a selected area of an electron microscope image. From these selected area electron diffraction patterns one can identify unknown contaminants or other particles as small as 2 microns across. The development of techniques in this field may be of considerable value in the study of lubricating oils and fuels, where it would be desirable to differentiate wear particles, carbon particles and additives.

Process Control

The application of the electron microscope in process or industrial control requires that the instrument provide the information that determines the end of a manufacturing process.

Research, correlation and development procedures, however, must be worked out before one can establish useful test routines that can be used for diagnosis and control. While we may safely assume that many industrial laboratories are concerned with applying the microscope to process control and may be successfully doing so in many instances, activities of this type cannot be evaluated by reading the literature. This is undoubtedly due to the fact that many laboratories are concerned with studying manufacturers' products, and while the results of these studies may be important to the manufacturer they may not be of sufficient general interest to warrant publication.

IN SUMMARY

The electron microscope is a useful tool in many fields of research. With it one can examine particles too small to be seen with the light microscope. The shape and structure of these particles become clearly visible because of the high resolving power of the electron microscope. Length, width, thickness and state of aggregation of particles can be determined. In other words, an investigator can obtain information relating to particle geometry.

It is not yet possible to define the limit of usefulness of the electron microscope. It has been in general use for only a few years and the possible applications of the instrument are still numerous and unpredictable. In spite of its relative newness among scientific instruments, however, the electron microscope is being used successfully in many laboratories. In the petroleum industry it is being applied especially to the study of the soap fibers in lubricating greases, additives in lubricating oils, catalyst particles and wear surfaces in bearings or other friction problems. In these fields significant results have been obtained relating the physical properties of petroleum products and the images seen in the electron microscope.

The foregoing account has shown that, as a tool of research, the electron microscope has taken an important place among the other scientific instruments. The limits of its application depend upon the imagination and ingenuity of the electron microscopist.

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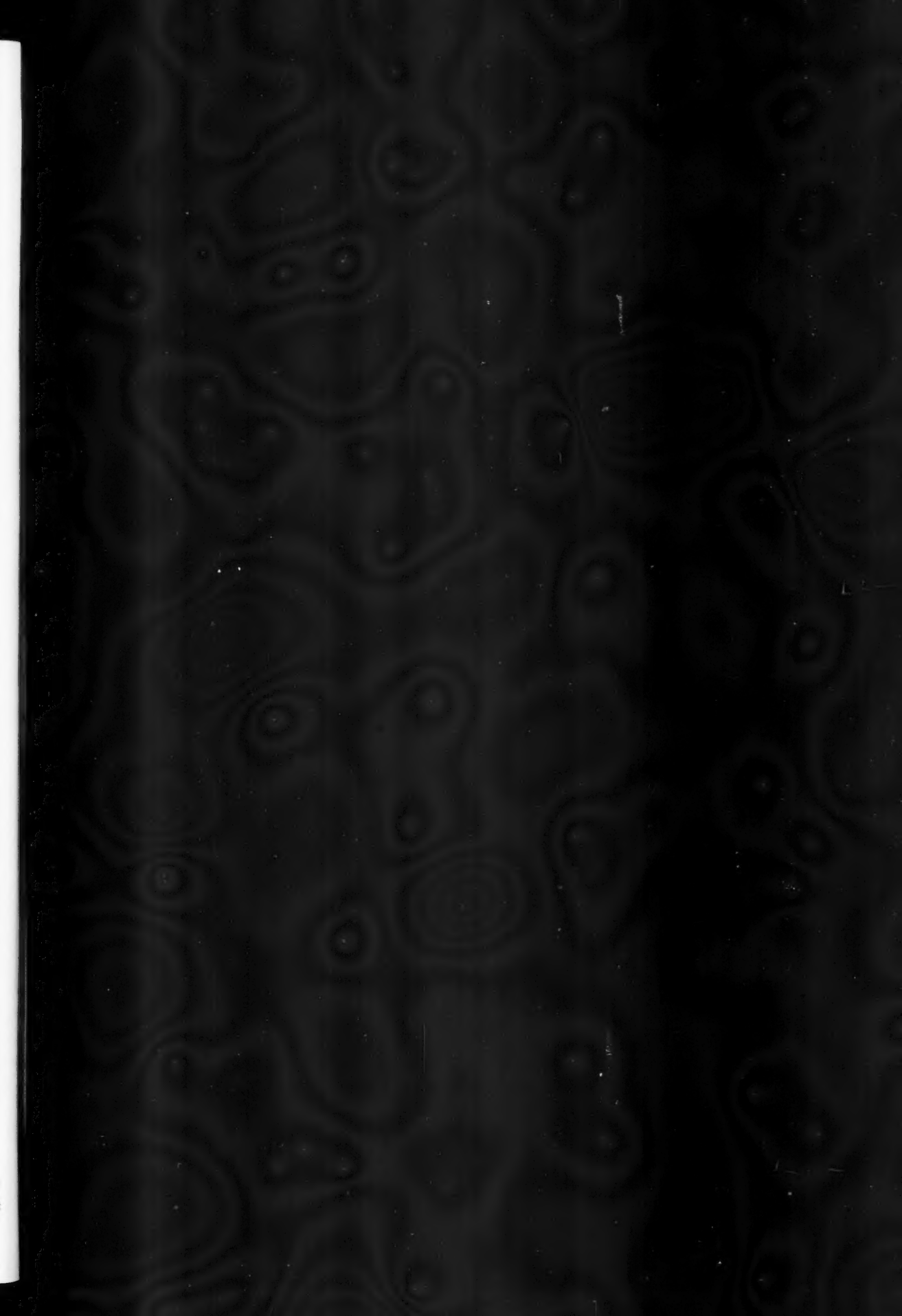

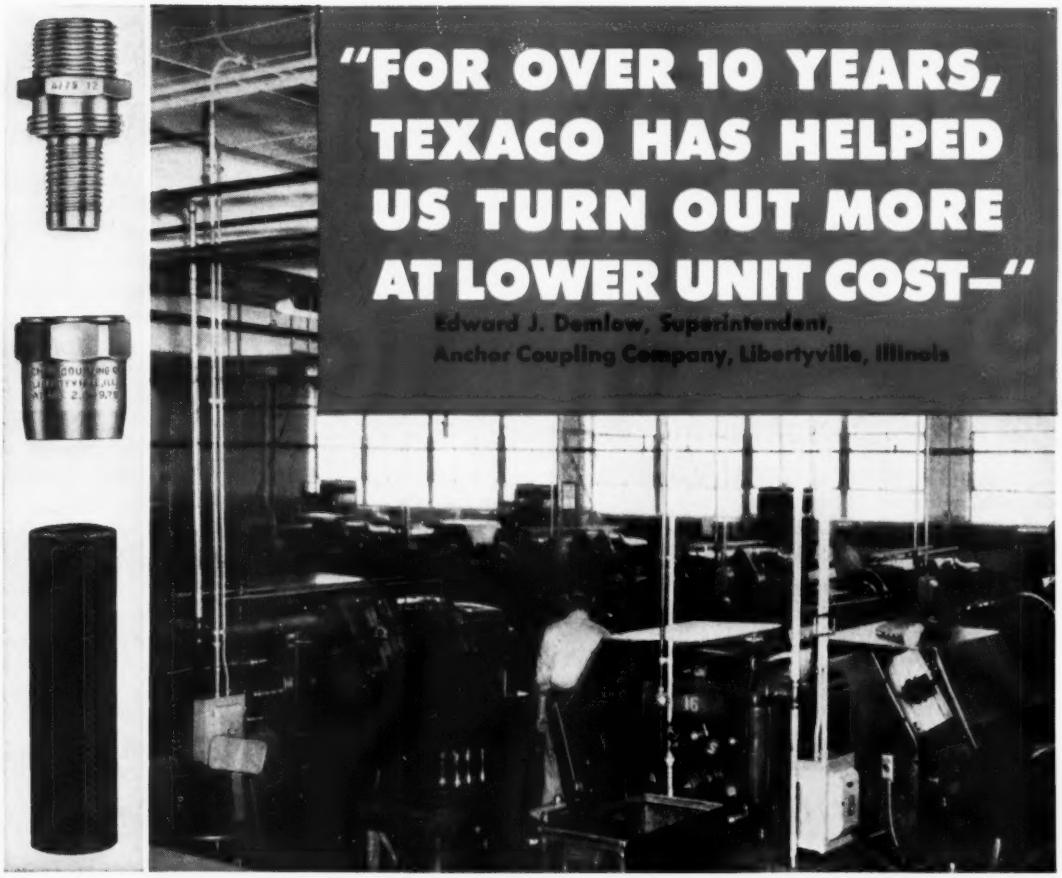

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